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Author(s):

Duncan W. McBranch*, Victor I. Klimov, Brett A. Kraabel, Eric S.
Maniloff, and Su Xu

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Ultrafast solid-state electron transfer in donor-acceptor conducting polymers

Duncan W. McBranch*, Victor I. Klimov, Brett A. Kraabel, Eric S. Maniloff, and Su Xu
CST-6. Los Alamos National Laboratory

Abstract

The objective of this project was to systematically study the nature of photoexcitations and the physics of electron transfer in donor-acceptor conducting polymer materials. Specifically we were interested in gaining a better understanding of the various steps involved in the charge transfer: the excitation events, the charge transfer itself, and the stabilization mechanism. We were largely successful in accomplishing these goals. We found that the initial photoexcitations in conjugated polymers were excitonic in nature, and the relaxation pathways were strongly dependent on the density of photogenerated species. We observed formation of bi-excitons at high excitation densities. In solid-state samples, bi-exciton states mediate charge separation of electron and hole polarons onto neighboring polymer chains. At lower excitation densities this channel becomes insignificant and the radiative relaxation is dominant. Our studies provide an explanation for experimental observations that charge transfer is linear in pump intensity in donor-acceptor blends and is a quadratic process in films of pristine polymers. We demonstrated that charge transfer in polymeric systems can be used for generation of transient gratings applicable, for example, in ultrafast image processing, optical switching, and beam steering.

Background and Research Objectives

Light-emitting polymers such as poly(*para*-phenylene vinylene) (PPV) have been intensively studied recently. The electronic and optical properties of these materials such as the energy gap and the emission wavelength can be tailored over a wide range by relatively simple chemical modifications of the molecular structure. This tunability makes polymers ideally suited for a variety of technological applications, including light emitters and lasers, elements of electronics and optoelectronics circuits, photovoltaic cells, and luminescent displays. Despite numerous investigations into the photophysics of π -conjugated polymeric systems, the nature and mechanisms of formation of the primary photoexcitations in these materials remain a matter of substantial controversy. It is widely accepted that in dilute solutions with weakly-interacting molecules, the dominant excitations are intrachain singlet excitons that have been described either as Coulombically bound electron-hole pairs or self-localized "polaron excitons".

*Principal Investigator, e-mail: mcbranch@lanl.gov

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In solid-state samples with strong inter-molecular interactions, ultrafast charge transfer can lead to the formation of non-emissive inter-chain species, sometimes referred to as "indirect excitons" or bound polaron pairs. These species have been cited by some authors as primary excitations in solid-state samples, although this point of view is not universally accepted.

Because of the controversy outlined above, the issue that we planned to address first in our project was to clarify the nature of primary photoexcitations in PPV-type polymers and to study mechanisms for formation of species which are not directly coupled to optical fields: electron (hole) polarons and "indirect" excitons. Once the understanding of nature of photoexcitations in pristine polymeric materials was developed we planned to move on to the next stage of the project, namely to studies of dynamics of photoinduced charge transfer in solid-state blends of donor-acceptor polymers and fullerenes. Of particular interest for us were a) identifying new transient spectral features arising from the charge transferred state, b) tracking the dynamics of structural deformation which occurs in conjunction with the charge separation and stabilization of the excited state; c) developing novel measurements of nonlinear optical effects arising from the large transient intrinsic electric fields resulting from ultrafast charge separation on a molecular length scale. An important component of the project was developing new chemically modified derivatives of the polymers and fullerenes for which the distinct steps in the charge transfer process are enhanced. The use of such derivatives should make it easier to distinguish between different stages of the charge transfer process and would allow a more precise control over the rate and the efficiency of charge separation. The synthetic work was performed in collaboration with researchers at the University of California at Santa Barbara, and the University of California at Los Angeles.

Importance to LANL's Science and Technology Base and National R&D Needs

The research conducted within this project was a combination of fundamental studies into a new class of electron transfer processes and applied research concerning technological applications of these processes. Our results on the nature of primary and secondary photoexcitations in polymers, and mechanisms of the photo-induced charge separation have a broad impact which we expect to extend into other areas of conducting polymers. An important accomplishment in this project was bridging the gap between research into photosynthetic reactions and research into conducting polymers, which allowed us to apply the concepts from a mature polymeric field into a newly emerging research area of charge transfer. The important technological implications of the research performed in the project was identifying mechanisms for photo-induced charge separation in films of pristine polymers. Charge separation leads to quenching of photoluminescence and thus results in degradation in the performance of polymer-based light-emitting devices.

Our results are of significant importance for several LANL programs concerned with development of novel soft-matter materials and studies of the nature and dynamics of electronic excitations in these materials. The work within the project allowed us to extend the funding base for our polymer studies outside LANL, leading in particular to a new program "Ultrafast holographic materials" funded through AFOSR. Additionally, our successful work on π -conjugated systems, combined with the work of our group on inorganic semiconductor nanoparticles have brought us to the position which allows us to strongly address emerging funding opportunities within the recently announced national initiative "NTR: Nanotechnology for the 21st century".

Scientific Approach and Accomplishments

Instrumentation

To study spectral signatures and dynamics of photoexcitations in polymers and polymer/fullerene donor-acceptor blends we used femtosecond (fs) pump-probe transient absorption (TA) experiment [1]. In this experiment, the transmission of the sample excited with a short pulse (typically 100 fs) was probed by delayed pulses of fs white-light continuum. The probe beam transmitted through the sample was dispersed with a spectrometer or a monochromator and was finally detected with either a charge-couple device (CCD) (which provides information on the entire TA spectrum) or a photodiode (single-wavelength detection). In the case of time-resolved sub-picosecond measurements, it is very important to account for temporal dispersion of the frequency (chirp) of the probe pulse. In typical fs experiments, the probe pulse is chirped such that the red portion of the pulse arrives at the sample before the blue portion. The chirp can be accounted for by post-measurement numerical corrections employed usually in case of CCD detection.

Another approach developed by our group [1] employs single wavelength phase-sensitive detection and spectral scanning with simultaneous adjustment of the time delay between pump and probe pulses. This technique allowed us to perform direct measurements of chirp-free TA spectra over the entire bandwidth of a white-light continuum probe (2.8 eV to 1 eV) with a high-sensitivity (up to 10^{-5} in differential transmission).

Universal spectroscopic signatures of excitons and charge-transfer photoexcitations in π -conjugated polymers

Conjugated polymers, most notably those belonging to the PPV family, are technologically promising materials due to the ease with which they may be processed and the wide range over which their optical and electronic properties may be chemically tuned.

Over the last decade numerous potential technological applications have been demonstrated, including electroluminescent devices (light-emitting diodes [2] and light-emitting electrochemical cells [3]), solid-state lasers [4], photodetectors [5], photovoltaic devices [6], transistors [7], and integrated optoelectronic devices. All of these technologies would benefit from a unified picture of the fundamental photophysics of conjugated polymeric solids, and although many groups have contributed towards this goal [8 -11], there is still not widespread agreement about such a general framework.

TA spectroscopy is a powerful tool for studying the fundamental photophysics of conjugated polymers, but the interpretation of TA experiments has been the subject of much debate. The transient photoinduced absorption (PA) features observed in PPV and its derivatives have been attributed variously to triplet excitons [12], polarons [13], singlet intrachain excitons [14] (also referred to as "singlet polaron excitons"), spatially-indirect excitons [15] (also referred to as polaron pairs), and biexcitons [16]. More recently, the species previously referred to as spatially-indirect excitons (polaron pairs) have been assigned by some authors as excimers [17]. There is also significant disagreement over what conditions govern the branching between different excitations, and whether various photoexcitations are photo-generated directly or in secondary processes. Site-selective fluorescence measurements [18] and photoluminescence quantum efficiency measurements [19] suggest that in excess of 90 % of the initial photoexcitations in thin films of some PPV derivatives (including unsubstituted PPV and cyano-substituted PPV) are singlet intrachain excitons. In studies of different PPV derivatives (MEH-PPV), other authors have concluded that only about 10 % of the initial photoexcitations are singlet excitons, with the majority being generated as spatially-indirect excitons [20] or excimers [21]. Several factors contribute to the disparity in experimental results, including widely-varying experimental conditions for each particular measurement (e.g. excitation density, wavelength, or polarization of the photo-exciting light), and the fact that the samples under study have varied considerably in fundamental ways, such as chemical structure and morphology (e.g. solutions, films cast from various solvents, or thermally-converted, insoluble films), or the degree of photochemical degradation.

While it would clearly be desirable to have similar experimental conditions for all TA measurements of PPV derivatives, this is not the case for the large volume of literature cited above, due principally to the continually-evolving nature of pulsed laser technology. It is now well established that the photoexcitation density is a crucial parameter in TA measurements, [22] since the decay dynamics in both solid samples and solutions vary strongly with changing excitation density, through a combination of nonlinear decay mechanisms [23] and nonlinear generation mechanisms [16, 24].

The degree of photochemical degradation of the sample also is known to be an important factor in determining the types of photoexcitations created and the relaxation pathways for these photoexcitations. The degradation has been attributed to scission of the conjugated chain (at the vinylene double bond) with corresponding formation of terminal carbonyl and aldehyde groups as a result of photo-oxidation or high-temperature thermal conversion. The formation of these defects destroys the extended conjugation of the polymer chains, and thereby eliminates the strong π - π^* absorption. In addition, these defects act as efficient quenching centers for singlet excitons, since the electro negative carbonyl group is a strong electron acceptor, leading to the dissociation of the exciton [14].

Another factor to consider in interpreting the various TA measurements is the effect the substituent groups that are added to the PPV backbone in order to improve solubility or to tune the electronic properties of the material. The effect of substituent groups on the electronic properties of these materials may be considerable, e.g. shifting the ground-state absorption and excited-state absorption and emission spectra dramatically [25] and independently [14], so that some derivatives display stimulated emission, while others may not. The substituent groups also play a role in determining the morphology of samples, which strongly affects the optical and electronic properties of solid films. Substituent groups may be added symmetrically or asymmetrically to the polymer backbone, with a dramatic influence on the degree of aggregation in the sample, the microscopic interchain packing density and the degree of crystallinity [26]. For a given PPV derivative, solid samples cast from different solvents, or from solutions of different concentrations, may have quite different morphological structure. Finally, even assuming that one uses the same PPV derivative and attempts to account for other experimental variables, experience has shown that different batches of the "same" polymer can give somewhat different results [14].

In light of the diversity of experimental results in the literature and the multitude of experimental factors responsible for this diversity, there is a critical need for a more general description of the fundamental photophysics in phenylene-based conjugated polymers—a description that applies to all members of this important class of materials. In our project we performed detailed spectral TA measurements of a number of PPV derivatives in various morphologies. The goal of these studies was to identify their common features and to develop a simple framework for describing properties that are general to the entire class of phenylene-based conjugated materials. The materials studied included several soluble PPV derivatives in either spun-cast film or solution-aggregate form, self-assembled films of thermally converted PPV, a PPV oligomer, and films of poly(9,9-dioctylfluorene) (PFO). The linear absorption spectra of these materials are shown in Figure 1.

In all of these materials, we find evidence of two different types of photoexcitations, singlet intrachain excitons and charge-separated excitations. The singlet intrachain excitons give rise to stimulated emission in the visible regime and a pair of excited-state PA bands in the near-infrared (see Figure 2) with dynamics that are strongly dependent on the initial excitation density. The PA signature of the charge-separated excitations is remarkably general to all the materials studied in our laboratory to date, and consists of a PA band that peaks in the red region of the visible spectrum, between the near-IR PA peak and the SE peak of the singlet exciton.

The properties of the emissive singlet excitons are now well documented. While these properties have been addressed by many authors for individual members of this family of materials, this work shows conclusively that the TA features of the excitons are common to the entire class of compounds. The main elements are as follows. The singlet intrachain excitons are directly created (<100 fs) following photoexcitation. The new, allowed excited-state transitions lead to strong PA bands, including the PA_{ex} band documented in detail in this work, and another PA band in the near-IR in the vicinity of 0.5 eV. The stimulated transition back to the ground state leads to an SE band, red-shifted from the main $\pi - \pi^*$ absorption due to a combination of energy relaxation within an inhomogeneous distribution of emitters, and intrinsic vibronic relaxation (Stokes' shift). These TA spectral features (PA and SE bands) share common dynamics and intensity-dependence. The exciton decay is dominated in pristine samples at low excitation densities by radiative decay with a time constant of order 1 ns. At higher excitation densities, strong nonlinear processes (biexciton generation, exciton-exciton annihilation, and amplified spontaneous emission) lead to rapid depopulation of the excitons either directly to the ground state or to the secondary, charge-separated species. The threshold for the onset of nonlinear relaxation processes is approximately 10^{15} cm^{-2} . This threshold fluence has been used to estimate the spatial extent of the excitons (~ 50 Angstroms), implying an exciton delocalized over many unit cells of the polymer. This is also a typical length scale for dipole-coupled Forster energy transfer processes.

The dynamics of the charge-separated species are essentially independent of the initial excitation density. In pristine polymers, the generation mechanism is a quadratic process, whereas in doped polymers it becomes a linear process (compare Figures 3 and 4). Several different species, including excimers, polaron pairs, or excitons that undergo dissociative electron transfer to electron-accepting defects or dopants, may all contribute to this photoinduced absorption, in proportions that are dependent on extrinsic factors such as sample morphology, excitation density and the degree of sample photochemical degradation. However, in light of the remarkable similarity of the PA signature across a range of different phenylene-based conjugated polymers, and, most importantly, between pristine samples and deliberately doped samples,

we believe that TA in the red region of the spectrum is primarily due to polarons (unbound charged carriers on the polymer).

Mid-IR photoinduced absorption features in π -conjugated polymers

We have extended the capabilities of the high-sensitivity chirp-free transient absorption spectrometer to cover the spectral range from 1.1 eV to 0.5 eV. This has allowed us to extend our studies of conjugated polymer photoexcitations and charge-transfer to a new spectral range that has been studied very little to date. In both a PPV derivative and a polyfluorene (PFO), we find a new IR PA band that corresponds to the singlet intrachain exciton. This is shown in Figure 5 for DP6-PPV. In addition, in PFO we find evidence in the IR spectral range of hot carriers.

We report the existence of a TA feature in the IR in DP6-PPV, which we call PA_{IR} . This feature shares the same dynamics, excitation density dependence and dynamic anisotropy as PA_{EX} , which is the PA for the exciton. The dynamics of the TA from 0.5 eV to approximately 1.3 eV are identical (see Figure 6), implying that a single photoexcited species dominates this part of the TA spectrum from the hundred femtosecond to the hundred picosecond time scale. Since PA_{EX} is known to be due to a transition from singlet intrachain excitons to higher excited states [27] we conclude that PA_{IR} is also due to a transition from singlet intrachain excitons to higher excited states.

Previous publications reported a TA feature in the IR in different PPV derivatives, also peaking near 0.5 eV [15]. However, the spectral range of these measurements did not include the region between approximately 0.5 and 1 eV, but instead covered the range below 0.5 eV and above approximately 1 eV. The present work bridges this gap and shows that the IR feature observed in these earlier works indeed peaks near 0.5 eV.

The assignment of PA_{IR} to the exciton is in agreement with Frolov et al. [28] who also found matching dynamics for PA_{IR} and PA_{EX} in a soluble PPV derivative. In contrast, Hsu and coworkers assign the IR feature they observe in a substituted PPV to a charge-separated species.[15] However, their assignment is based on the matching dynamics of the red tail of the PA_{IR} feature (at 0.29 eV) with those of the TA feature at 1.5 eV. Hence it is not clear from their published results whether the entire PA_{IR} band follows the same dynamics as the visible TA band. Results obtained in our laboratory with a different phenylene-based conjugated polymer, poly(9,9-dioctylfluorene) (PFO), indicate that two distinct PA bands exist near 0.5 eV in this material, with the lower energy band decaying more slowly than the higher energy band [29].

In view of the fact that the charge-separated species PA_{CS} decays more slowly than the excitons PA_{CS} , and the similarity of many phenylene-based conjugated polymers, these results in PFO suggest the possibility that another PA_{IR} band may exist in DP6-PPV, but below the minimum probe energy of this measurement (0.5 eV).

Further comparison of the PA_{IR} band observed in this work with that observed by Hsu et al. [15] is hindered due to the different experimental parameters. For example, the TA spectrum published by Hsu et al. is for a 200 ps pump-probe delay time, leaving open the question of how the spectrum evolves over the first 200 ps. In addition, no mention of the excitation density used is made in their report, although it is now established that excitation density plays a significant role in determining the branching ratio between excitons and charge separated photoexcitations.[16, 24, 30] In the work of Hsu et al. they show that the dynamics of the SE do not match those of PA_{EX} , which is generally considered a sign of either a degraded sample, or excitation densities above the saturation limit for singlet intrachain excitons [27]. Thus, although it is apparent from their results that a TA band exists in the IR that is related to a charge separated species, the observation of this band may depend on the quality of the sample used and on the excitation density used. In the present work no evidence is found to relate PA_{IR} to PA_{CS} (the charge separated species) in DP6-PPV films.

Biexcitons in π -conjugated polymers and their role in charge-transfer

An issue which has been actively debated recently is the existence of coherent many-particle states such as cooperatively-emitting excitons and biexcitons. Biexcitons have been extensively studied in inorganic semiconductors. They were first detected experimentally in wide-gap materials, such as CdS and CuCl by their signatures in photoluminescence (PL) spectra. One of the effects associated with formation of biexcitons is the enhancement of the oscillator strength of the exciton-biexciton transition due to coherent interactions of two excitons; this is analogous to the effect of giant oscillator strength observed for excitons weakly bound to an impurity. The observation of excitons in inorganic semiconductors is hindered by their small binding energies that are typically in the range of several meV. Theoretical calculations show that the biexciton binding energy can be enhanced in quantum confined systems which has been confirmed experimentally by measurements of semiconductor quantum-dot structures. Several theoretical papers have suggested the existence of biexcitons in organic π conjugated systems, but clear experimental verification of biexcitons as a general feature in these materials is still lacking. Multi-exciton states have been observed in organic charge-transfer crystals. The superlinear growth of stimulated emission at high intensities in luminescent conjugated polymers has been attributed to cooperative emission, possibly due to biexcitons.

However, there is now widespread agreement that this effect is due solely to amplified spontaneous emission. A short-lived photoinduced absorption feature in a thiophene oligomer has been attributed to an "intermolecular biexciton state", but without any systematic investigation of its dynamics and intensity-dependence. Hence, it remains unclear under what conditions biexcitons are created, what their effects are on nonlinear absorption, and whether the properties of biexcitons in organic systems are similar to those in inorganic semiconductors.

In our work, we applied methods of fs TA to provide the first experimental demonstration of the existence of stable biexcitons in π -conjugated molecules [16]. To evaluate the role of intermolecular interactions at high excitation densities, we studied two different forms of the same material: dilute solutions and solid-state films. Our results demonstrate that in solutions, at low pump densities, both the stimulated emission (SE) and the photo-induced absorption (PA) can be explained in terms of generation of a single species – intra-chain singlet excitons. With increasing pump-intensity, the TA of solution samples clearly exhibits signatures of interaction between photoexcitations occupying a single chain, which we attribute to formation of stable biexcitons with oscillator strength enhanced due to coherent interaction of two excitons. We also observe biexciton signatures in films. However, due to strong intermolecular interactions, two-exciton states in films are unstable and decay on the sub-ps time scale with formation of inter-chain species.

Ultrafast holography using charge-transfer polymer blends

Holographic gratings have attracted interest for applications such as interconnection networks, 3-D optical data storage and optical computing [31]. Although the most widely studied materials have been inorganic photorefractive materials, recently organic holographic materials such as photorefractive polymers, photochromic molecules, and conjugated polymers have received increased attention. Typically materials present a trade-off between rapid response time and high diffraction efficiency. The materials with the largest diffraction efficiencies have been photorefractives, but the response time of these materials is on the time scale of seconds. Third order nonlinear optical materials have essentially instantaneous response times, but are plagued by low diffraction efficiencies. Conjugated polymers provide a unique class of materials which combine fast response times (subpicosecond) with high diffraction efficiencies. In addition, the response time of these materials can be tuned from picoseconds to hundreds of picoseconds by blending them with electron acceptors such as C_{60} .

We investigated the diffraction efficiency of poly(2,3-diphenyl-5-hexyl-p-phenylene vinylene) (DP6-PPV) and of DP6-PPV and poly[2-methoxy,5-(2'-ethylhexoxy)-1,4-phenylene vinylene] (MEH-PPV) blended with cholestanoxymethanofullerene (PCBM) or C_{60} using broadband non-degenerate four-wave mixing.

In order to compare the results with those previously published we use the temporal diffraction efficiency (TDE) as a figure-of-merit. The TDE is defined as η/τ where η is the diffraction efficiency and τ is the time constant governing the holographic buildup.

The maximum diffraction efficiency we obtained was 1% for a thick ($\alpha d > 6$) film of DP6-PPV, which is similar to what was observed in MEH-PPV[32]. This occurs at a wavelength of approximately 900 nm. This gives a TDE of $0.01/10^{-13} \text{ s} = 10^{11} \text{ s}^{-1}$. This is two orders of magnitude larger than that reported for other third-order nonlinear polymer experiments, 11 orders of magnitude larger than the best photorefractives, and 12 orders of magnitude larger than results reported for photo-isomerization.

Summary

In our project, we have performed detailed studies on ultrafast photoinduced processes in a number of conjugated polymers belonging to poly(*para*-phenylene vinylene) (PPV) family and in polymer-fullerene blends. Our results provide strong evidence that two types of photoexcitations are created which are general to all polymers of the PPV family. These photoexcitations are the primary intrachain singlet excitons and a secondary species created at the expense of the excitons. We attribute the secondary species to weakly coupled charge-separated polarons. We observe that the rate of formation of charge separated polarons is quadratic with respect to the density of intrachain excitons, indicating a formation mechanism mediated by doubly-excited polymer (oligomer) chains, i.e. by *bi-excitons*. The bi-excitons are unstable in closely-packed polymer films and decay with formation of charged polarons on the sub-picosecond time scale due to inter-molecular interactions. Bi-excitons can be stabilized in dilute solutions for which intra-molecular interactions are suppressed. In solution samples, bi-excitons are manifested due to their enhanced oscillator strength leading to a superlinear growth of the stimulated emission and an accelerated decay at high pump densities. These studies have resolved a long-standing controversy concerning the mechanisms for charge separation in films of pristine polymers. In contrast to pristine films, the efficiency of charge separation in donor-acceptor polymer-fullerene blends is linear in pump intensity. By using different polymer and fullerene derivatives we were able to control the charge transfer time from sub-picoseconds to several hundreds of picoseconds which allowed a wide range tuning of charge-separation efficiencies. We demonstrate that charge separation in pristine polymer films and in polymer-fullerene blends can be used for generation of transient gratings applicable, for example, in systems for ultrafast image processing, optical switching, and beam steering.

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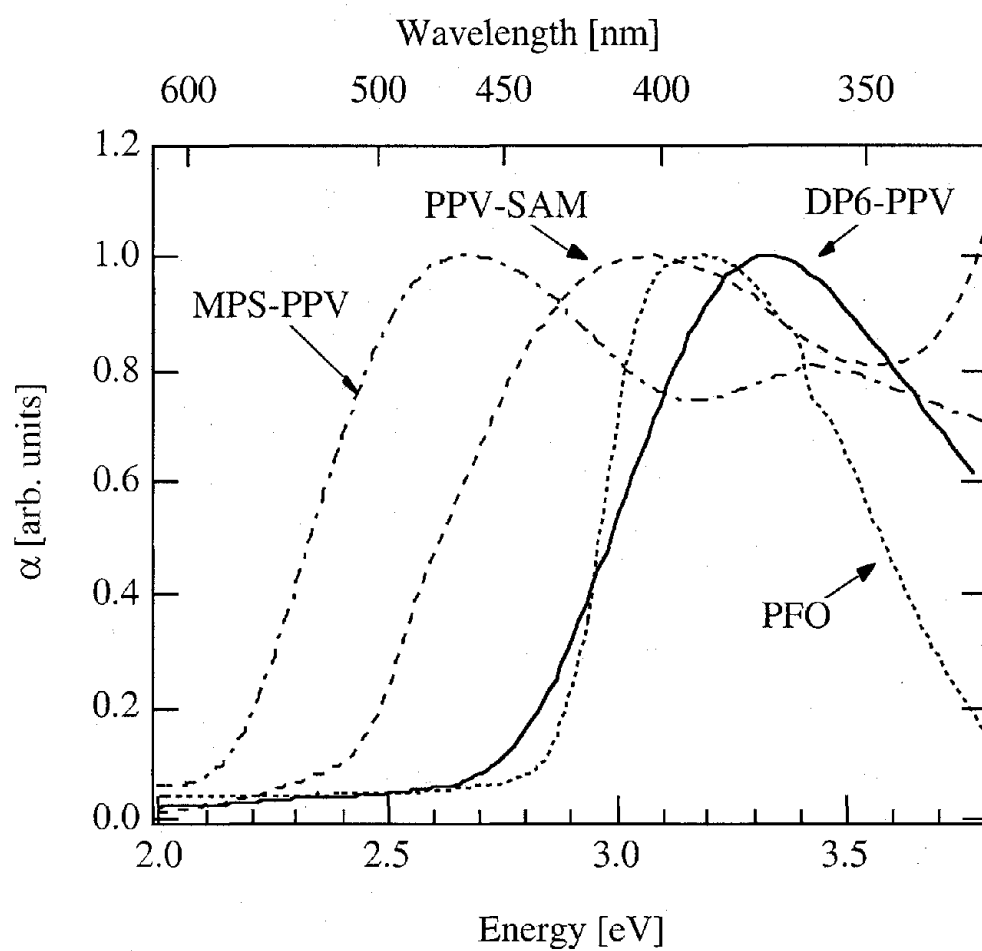


Figure 1

The linear absorption spectra of the materials discussed in this report.

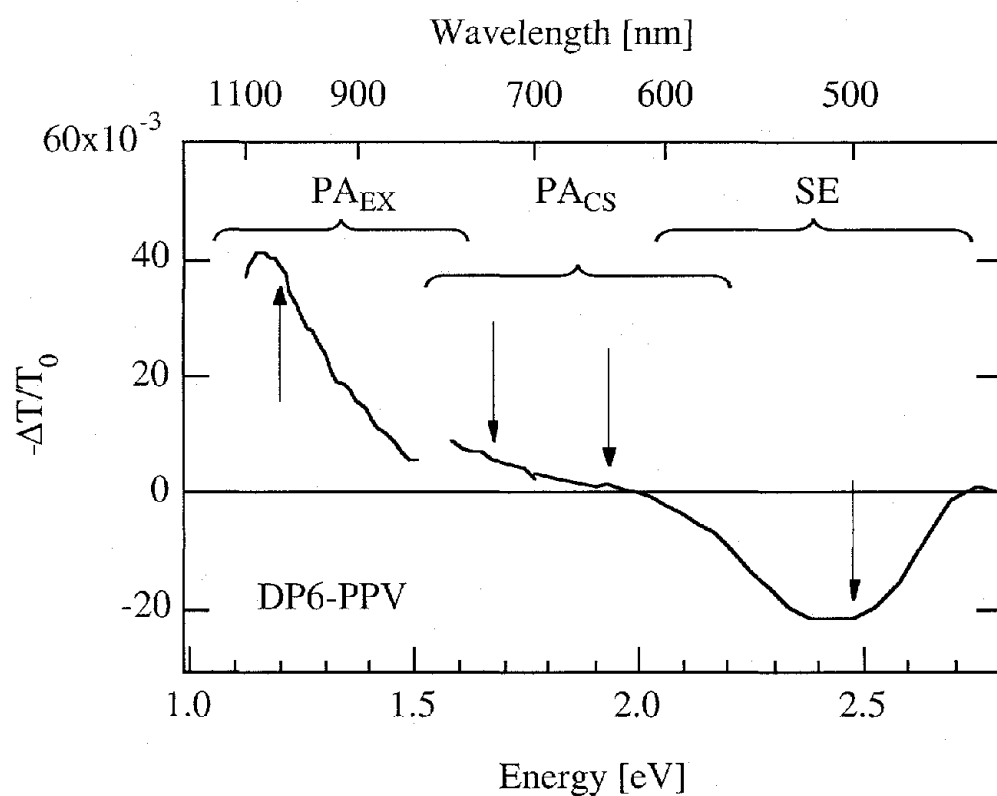


Figure 2

The chirp-free transient absorption spectrum of DP6-PPV with a pump-fluence of 10^{18} cm^{-3} . The arrows mark the regions where the dynamics and pump-fluence dependence were measured. The spectral regions of PA_{EX} , PA_{CS} and SE are also indicated.

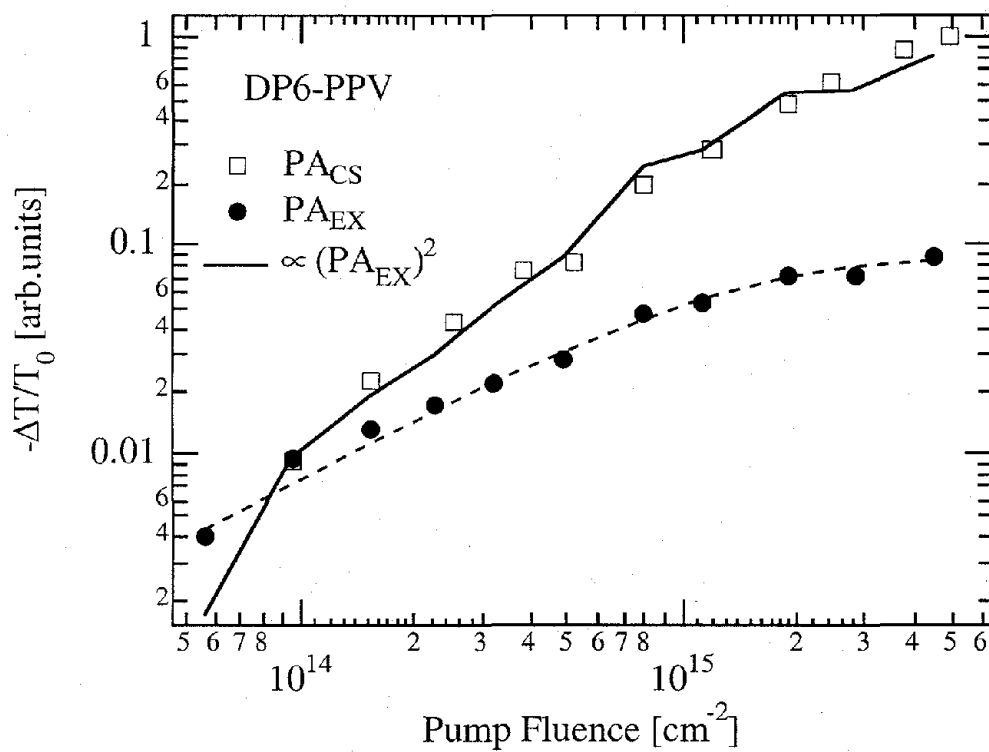


Figure 3

The pump-fluence dependence of PA_{EX} (solid circles) and of PA_{CS} (open squares) in DP6-PPV.

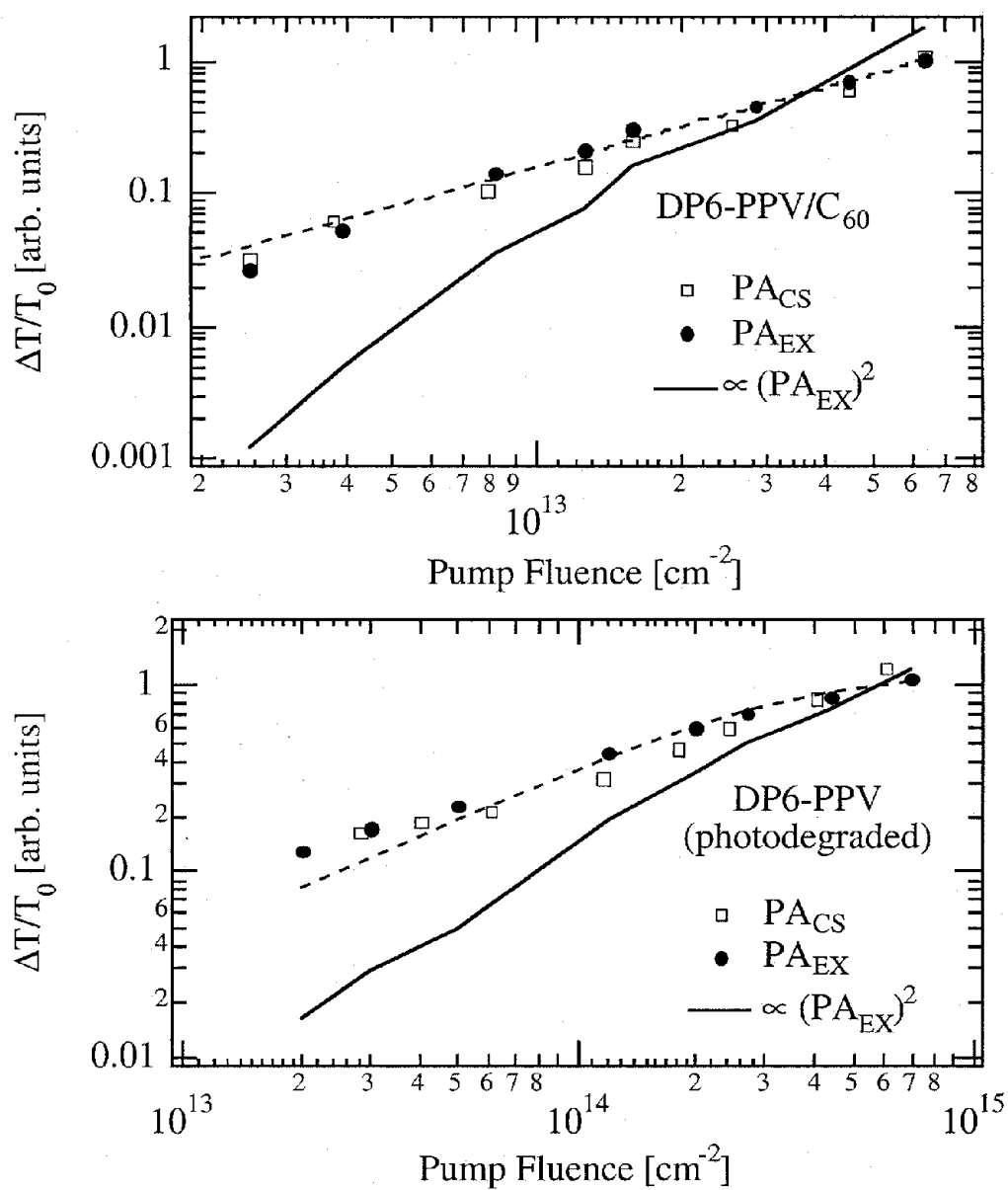


Figure 4

The dependence of PA_{EX} (solid circles) and PA_{CS} (open squares) on pump fluence for DP6-PPV/C₆₀ (top panel) and photodegraded DP6-PPV (bottom panel).

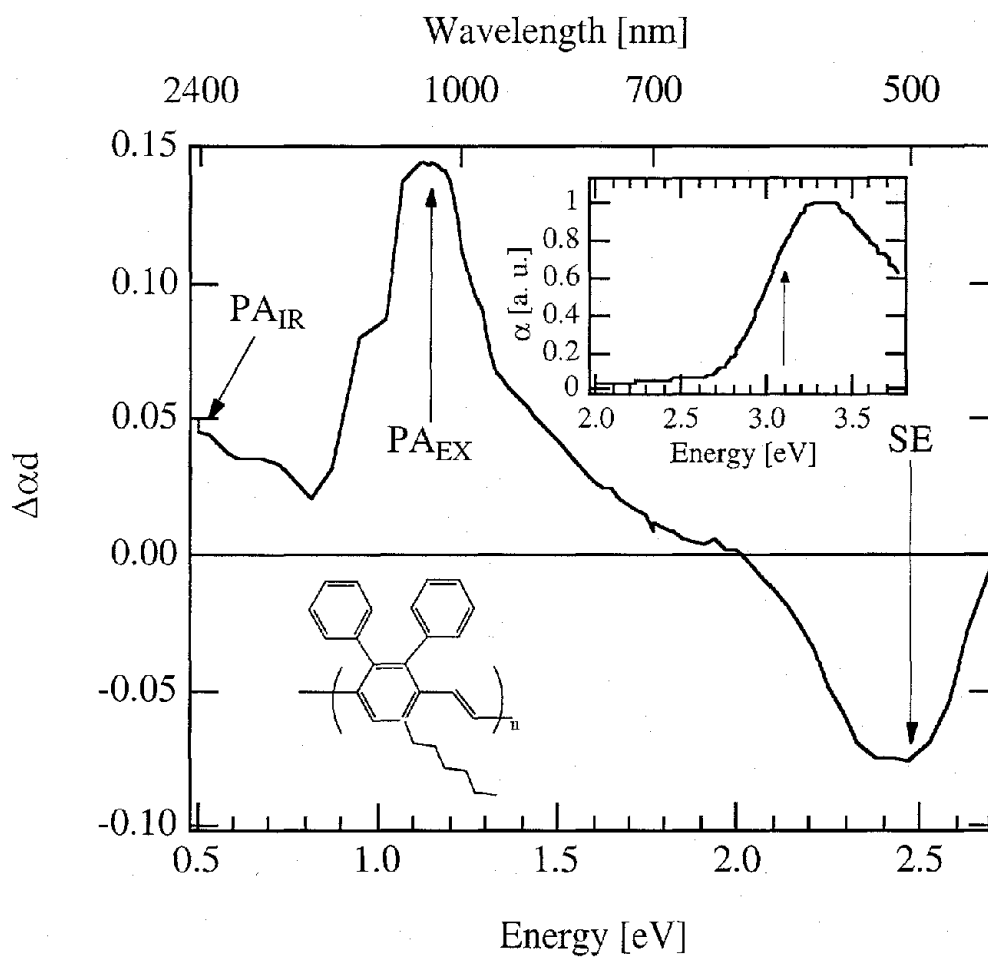


Figure 5

The transient absorption spectrum of DP6-PPV at < 1 ps delay time, using a photoexcitation density of 10^{18} cm^{-3} . The arrows labeled PA_{IR} , PA_{EX} and SE denote the energy where single wavelength measurements were made. The insets show the chemical structure of DP6-PPV and the linear absorption spectrum.

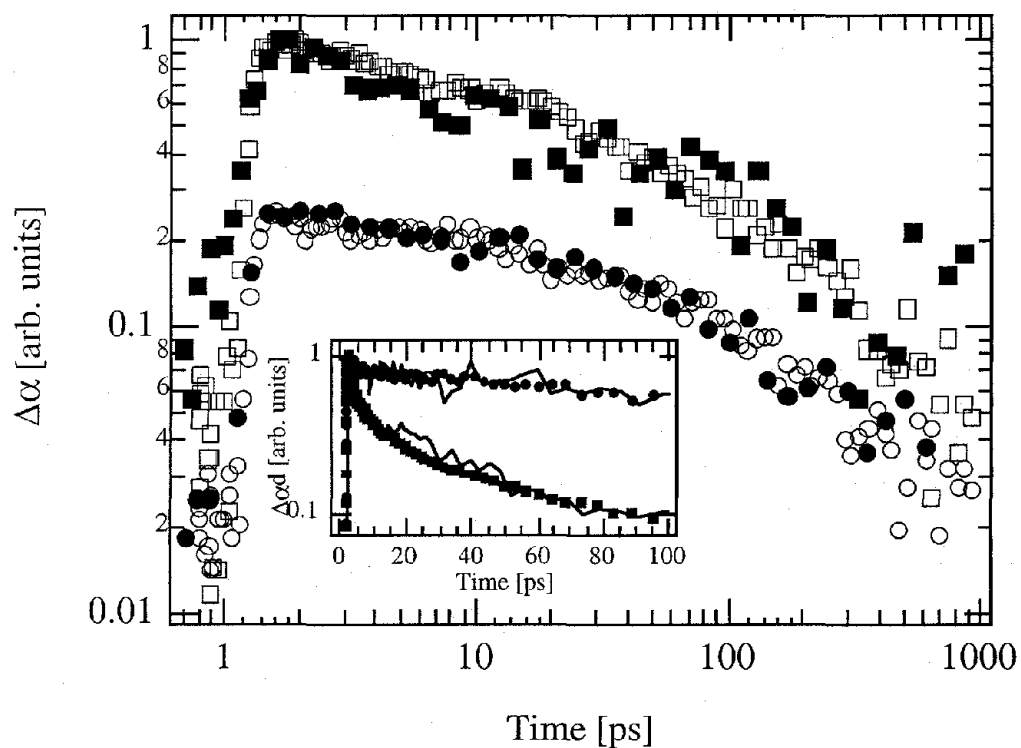


Figure 6

The dynamics of PA_{IR} (solid symbols) and PA_{EX} (open symbols) for excitation densities of 10^{18} (circles) and 10^{19} (squares) cm^{-3} . The data (and the time axis) are offset for clarity. The inset shows the dynamics of PA_{EX} and SE for excitation densities of 10^{17} and 10^{19} cm^{-3} .